

# Dynamical Screening and Superconducting State in Intercalated Layered Metallochloronitrides

A. Bill\*

Paul Scherrer Institute, Condensed Matter Theory, 5232 Villigen PSI, Switzerland

H. Morawitz

IBM Almaden Research Center, 650 Harry Rd., San Jose, CA 95120, USA

V.Z. Kresin

Lawrence Berkeley Laboratory, University of California at Berkeley, CA 94720, USA

An essential property of layered systems is the dynamical nature of the screened Coulomb interaction. Low energy collective modes appear as a consequence of the layering and provide for a superconducting-pairing channel in addition to the electron-phonon induced attractive interaction. We show that taking into account this feature allows to explain the high critical temperatures ( $T_c \sim 26\text{K}$ ) observed in recently discovered intercalated metallochloronitrides. The exchange of acoustic plasmons between carriers leads to a significant enhancement of the superconducting critical temperature that is in agreement with the experimental observations.

PACS numbers: 74.70.-b, 74.70.Dd, 74.20.Mn, 74.20.-z

Screening of the Coulomb interaction takes very different forms in layered conductors and three dimensional (3D) isotropic metals. We show that the dynamic screening in layered systems can lead to a Coulomb induced enhancement of the superconducting pairing and might be an essential addition to the usual electron-phonon contribution. This important feature results from the existence of low energy electronic collective modes characteristic for layered materials.

The aim of the present paper is to explain the nature of the superconducting state in layered intercalated metallochloronitrides [1]. It has been shown that intercalation of metallic ions and organic molecules into the parent compound (Zr,Hf)NCl leads to a superconductor with rather high critical temperature ( $T_c \sim 26\text{K}$ ) [1]. Based on experimental studies [1, 2, 3, 4, 5, 6, 7] and band structure calculations [8, 9] it was concluded that 1) electron-phonon mediated pairing is insufficient to explain the high  $T_c$ s observed and that 2) there is no evidence for the presence of strong correlations; the system can be described within Fermi liquid theory. In addition, these compounds do not have magnetic ions which excludes a magnetic mechanism as well. No explanation has been suggested so far as to what pairing mechanism can allow to reach the observed critical temperatures. The theory proposed below shows that such high  $T_c$ s can be obtained by including the additional pairing contribution arising from the interaction of carriers with acoustic plasmons; this is the manifestation of the dynamic screening effect of the Coulomb interaction.

The description of layered conductors can be made by neglecting the small interlayer hopping in first approximation. On the other hand, it is essential to take into account the screened interlayer Coulomb interaction which has an important dynamic part. Indeed, it is known that for usual 3D materials this interaction can be considered in the static limit since electronic collective modes are very high in energy (the

optical plasmon energies are of the order 5-30eV in metals; see, e.g., [10].) Therefore, the Coulomb repulsion enters the theory of superconductivity as a single constant pseudopotential  $\mu^*$ . The situation is very different in layered conductors: incomplete screening of the Coulomb interaction results from the layering [11]. The response to a charge fluctuation is time-dependent and the frequency dependence of the screened Coulomb interaction becomes important. This leads to the presence of *low* energy electronic collective modes: the acoustic plasmons. It is this particular feature of layered materials that brings about an additional contribution to the pairing interaction between electrons.

The order parameter  $\Delta(\mathbf{k}, \omega_n)$  of the superconducting state is described by

$$\Delta(\mathbf{k}, \omega_n) Z(\mathbf{k}, \omega_n) = T \sum_{m=-\infty}^{\infty} \int \frac{d^3 \mathbf{k}'}{(2\pi)^3} \Gamma(\mathbf{k}, \mathbf{k}'; \omega_n - \omega_m) F^\dagger(\mathbf{k}, \omega_m), \quad (1)$$

where  $F^\dagger = \langle c_{k,\uparrow}^\dagger c_{-k,\downarrow}^\dagger \rangle$  is the Gor'kov pairing function) and  $Z(k, \omega_n)$  is the renormalization function, defined by

$$Z(\mathbf{k}, \omega_n) - 1 = \frac{T}{\omega_n} \sum_{m=-\infty}^{\infty} \int \frac{d^3 \mathbf{k}'}{(2\pi)^3} \Gamma(\mathbf{k}, \mathbf{k}'; \omega_n - \omega_m) G(\mathbf{k}, \omega_m). \quad (2)$$

$G = \langle c_{k,\sigma}^\dagger c_{k,\sigma} \rangle$  is the usual Green function, and  $\Gamma$  the total interaction kernel;  $\omega_n = (2n+1)\pi T$ . We use the thermodynamic Green's functions formalism (see e.g. Ref. [12]). The  $T_c$  for layered superconductors is obtained by solving the set of equations (1,2) self-consistently.

The interaction kernel is composed of two parts,  $\Gamma = \Gamma_{ph} + \Gamma_c$ , where

$$\Gamma_{ph}(\mathbf{q}; |n-m|) = |g_v(\mathbf{q})|^2 D(\mathbf{q}, |n-m|) \quad (3)$$

$$\Gamma_c(\mathbf{q}; |n-m|) = \frac{V_c(\mathbf{q})}{\epsilon(\mathbf{q}, |n-m|)}. \quad (4)$$

\*Electronic address: abill@psi.ch

The first term,  $\Gamma_{ph}$ , is the usual pairing contribution resulting from the electron-phonon interaction.  $D(q, n-m) = \Omega_v^2(q)[\omega_n - \omega_m]^2 + \Omega_v^2(q)]^{-1}$  is the phonon temperature Green's function,  $\Omega_v(q)$  the phonon frequency; summation over phonon branches  $v$  is assumed. The second contribution to the interaction kernel,  $\Gamma_c$ , is the Coulomb part written in its most general form as the ratio of the bare Coulomb interaction  $V_c(\mathbf{q})$  and the dielectric function  $\epsilon(\mathbf{q}, \omega_n - \omega_m)$ . Both functions have to be calculated for a layered structure.

The Coulomb interaction for conducting layers separated by spacers of dielectric constant  $\epsilon_M$  can be written in the form [11, 13]:

$$V_c(\mathbf{q}) = \frac{2\pi e^2}{\epsilon_M q_{\parallel}} R(q_{\parallel}, q_z) = \frac{\lambda_c}{N(E_F)} \tilde{V}_c(q_{\parallel}; q_z), \quad (5)$$

where  $q_{\parallel}(q_z)$  is the in-plane (out-of-plane) component of the wave-vector. In the last expression,  $N(E_F)$  is the 2D electronic density of states (DoS) at the Fermi energy  $E_F$ , and  $\tilde{V}_c(\mathbf{q}_{\parallel}; q_z) = R(q_{\parallel}, q_z)/(2k_F q_{\parallel})$  with

$$R(q_{\parallel}, q_z) = \frac{\sinh(q_{\parallel} L)}{\cosh(q_{\parallel} L) - \cos(q_z L)}. \quad (6)$$

$L$  is the interlayer spacing and  $\lambda_c = (e^2/\hbar v_F)/2\epsilon_M$  is the dimensionless Coulomb interaction constant ( $v_F$  is the Fermi velocity). The dielectric function  $\epsilon(\mathbf{q}, \omega_n - \omega_m)$  has been calculated for a layered system [13, 14, 15] in RPA. It has been shown there that the plasmon spectrum contains anisotropic bands  $\omega_{pl} = \omega_{pl}(\mathbf{q}_{\parallel}, q_z)$  that can be labeled by  $q_z$  and which are the low frequency acoustic modes.

Eqs. (1,2) can be cast into the following matrix form near  $T_c$  (see our paper, Ref. [15])

$$\sum_m \sum_{k'_z} K_{n,m}(|q_z|) \Phi_m(k'_z) = \eta \Phi_n(k_z) \quad , \quad (7)$$

where  $q_z \equiv k_z - k'_z$  are the wave-vector components normal to the conducting layers and  $\Phi_m(k'_z) = \Delta_m(k'_z)/\sqrt{2m+1}$  is the reduced order parameter. In the case of a layered superconductor, the matrix  $K$  takes the form

$$K_{n,m}(|q_z|) = \frac{1}{N_z} \frac{1}{\sqrt{2n+1}\sqrt{2m+1}} \left\{ \begin{aligned} &\lambda [D(n-m) + D(n+m+1)] \\ &+ \lambda_c [\Gamma_c^I(n-m; |q_z|) + \Gamma_c^I(n+m+1; |q_z|)] \\ &- \mu^* \theta(\Omega_c - |\omega_m|) \\ &- \delta_{n,m} \sum_{p=0}^{2n} [\lambda D(n-p) + \lambda_c \Gamma_c^I(n-p; |q_z|)] \end{aligned} \right\} . \quad (8)$$

$n-m$  is short hand for the difference of Matsubara frequencies  $\omega_n - \omega_m = 2\pi \tilde{T}(n-m)$  [with  $\tilde{T} = k_B T/\Omega$ ; we consider an Einstein phonon  $\Omega_v(\mathbf{q}) \equiv \Omega$ ].  $\Omega_c$  is the cutoff used to define the pseudopotential  $\mu^*$ , and  $N_z$  is the number of  $q_z$ -points considered in the Brillouin zone. All but the static Coulomb

repulsion  $\mu^*$  are temperature dependent quantities. The critical temperature of the superconducting phase-transition  $T_c$  is reached when the highest eigenvalue is  $\eta = 1$ .

$\Gamma_c^I(n, |q_z|)$  is the frequency-dependent contribution of the screened Coulomb interaction arising from acoustic plasmons. It has been shown by two of the authors, I. Bozovic, G. Rietveld, and D. van der Marel [14] that the density of states (DoS) of the low-energy collective modes is peaked at  $q_z = \pi$  and  $q_z = 0$ . Furthermore, it was demonstrated that the  $q_z = 0$  term is repulsive and can therefore be included into the pseudopotential  $\mu^*$  [15]. The main plasmon contribution to the pairing is thus obtained for  $q_z = \pi/L$  and has the form

$$\Gamma_c^I(n-m) = \frac{\lambda_c}{2\pi} \int_0^{\tilde{q}_c} \frac{d\tilde{q}}{\sqrt{1-\tilde{q}^2}} \frac{\tilde{V}_c(\tilde{q})}{\epsilon(\tilde{q}, n-m)}, \quad (9)$$

where  $\tilde{q} \equiv q_{\parallel}/2k_F$ , and  $\tilde{q}_c = \min\{1, |\omega_n - \omega_m|/4E_F\}$  divides  $(\omega, q)$ -space into the regions  $\omega > qv_F$  and  $\omega < qv_F$ . The first region corresponds to the dynamic response and contains plasmon excitations, including the acoustic plasmon branches. In the second region the response can be treated in the static approximation and represents the usual repulsive part of the screened Coulomb interaction. We calculate the value of the critical temperature from Eqs. (7-9).

In order to demonstrate the importance of dynamic screening for superconductivity we calculate  $T_c$  for the following set of realistic parameters:  $L = 15\text{\AA}$ ,  $\lambda = 0.5$ ,  $\Omega = 70\text{meV}$ ,  $\epsilon_M = 3$ ,  $v_F = 5 \times 10^7$ ,  $\mu^* = 0.1$ ,  $m^* = m_e$ . As will be seen below, these values are close to those found in metallochloronitrides. With these parameters, the Coulomb interaction constant defined earlier is  $\lambda_c = 0.6$ . One can, therefore, use RPA in a first approximation and neglect vertex corrections.

With use of aforementioned values for the three quantities  $\lambda$ ,  $\Omega$  and  $\mu^*$  one can, in a first step, calculate the value  $T_{c,ph}$  which is the critical temperature in the absence of dynamic screening ( $\Gamma_c^I = 0$ ). One obtains  $T_{c,ph} = 12\text{K}$ . If we now take into account the effect of dynamic screening and calculate  $T_c$  using all parameters given above, we obtain  $T_c = 25\text{K}$ . This demonstrates that the value of  $T_c$  in layered superconductors can be drastically affected (enhanced) by the dynamic part of the screened Coulomb interaction.

We now apply our approach to a specific case among intercalated metallochloronitrides. Namely the compound  $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$  which has a  $T_c = 25.5\text{K}$  [1]. We selected this compound as a study case because there has been relatively detailed experimental and theoretical work done on this layered material. From Ref. [5, 6] the interlayer distance  $L$  and characteristic phonon frequency  $\Omega$  are equal to  $L = 18.7\text{\AA}$  and  $\Omega = 60\text{meV}$ , respectively. The effective mass and Fermi energy have been estimated from band structure calculations [8]. Accordingly,  $m^*/m_e \simeq 0.6$  where  $m_e$  is the free electron mass and  $E_F \simeq 1\text{eV}$ . Finally, according to Ref. [6] we take  $\mu^* = 0.1$ . Selecting the values  $\epsilon_M = 1.8$  and  $\lambda = 0.3$  and calculating  $T_c$  with Eqs. (3-9), we obtain  $T_c = 24.5\text{K}$ , which is close to the experimental value [1]. In absence of the plasmon part ( $\Gamma_c^I = 0$ ) we obtain  $T_{c,ph} = 0.5\text{K}$  which indeed confirms that the conventional electron-phonon mechanism cannot explain the high critical temperature observed in this material.

TABLE I: Determination of  $T_c$  ( $T_{c,ph}$ ) in presence (absence) of the contribution due to dynamic screening of the Coulomb interaction. The parameters are those taken for  $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$ ;  $\mu^* = 0.1$ ,  $\Omega = 60\text{meV}$ ,  $m^*/m = 0.6$ ,  $E_F = 1\text{eV}$ ,  $L = 18.7\text{\AA}$

$\lambda$	$\epsilon_M$	$T_{c,ph}[\text{K}]$	$T_c[\text{K}]$
0.5	2.2	11	24.9
0.4	1.95	4.3	25.3
0.3	1.8	0.5	24.6

We point out that the calculation just performed for  $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$  makes use of reasonable, but still adjustable parameters  $\lambda$  and  $\epsilon_M$ . A more detailed analysis requires the experimental determination of these quantities prior to our calculation. It would thus be of interest to perform tunneling measurements which would allow to determine the function  $\alpha^2(\Omega)F(\Omega)$  [ $F(\Omega)$  is the phonon density of states whereas  $\alpha^2(\Omega)$  describes the coupling], and correspondingly  $\lambda$  (along with  $\mu^*$ ; see, e.g., Refs. [16, 17]). Another method to determine  $\lambda$  requires to measure the electronic heat capacity.

Indeed, as is known, the Sommerfeld constant contains the renormalization factor  $1 + \lambda$  while the magnetic susceptibility is unrenormalized (see, e.g., Ref. [17]). Comparing these two quantities one can extract the value of the coupling constant  $\lambda$ . Such measurements, along with optical data would allow to carry out more detailed calculations of  $T_c$  for specific metallochloronitrides.

In absence of such experimental data, we present in table I a few typical examples of calculated  $T_c$  for various realistic values of the parameters  $\lambda$  and  $\epsilon_M$  in  $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$ .

Note that in all cases the optical plasmon energy at  $\mathbf{q} = 0$  is of the order  $\omega_{pl,opt}(\mathbf{q} = 0) \simeq 1 - 1.3\text{eV}$ , in agreement with band structure calculation estimates. A more detailed analysis of other metallochloronitrides will be described elsewhere.

In conclusion, the dynamical screening of the Coulomb interaction is an essential feature of layered structures that provides for an additional contribution to the pairing and leads to a drastic enhancement of  $T_c$ . The theory presented here enables us to give an explanation for the high critical temperatures observed in intercalated layered metallochloronitrides.

- 
- [1] S.Yamanaka, K.-I.Hotahama, and H.Kawaji, *Nature* **392**, 580 (1998); S. Yamanaka, H. Kawaji, K.-I. Hotahama, and M. Ohashi, *Adv. Mater.* **8**, 771 (1996).
  - [2] H. Kawaji, K. Hotahama, and S. Yamanaka, *Chem. Mater.* **9**, 2127 (1997).
  - [3] S. Shamoto, T.Kato, Y.Ono, Y.Miyazaki, K.Ohoyama, M.Ohashi, Y.Yamaguchi, and T.Kajitani, *Physica C* **306**, 7-14 (1998).
  - [4] S. Shamoto, K. Iizawa, M. Yamada, K. Ohoyama, Y. Yamaguchi, and T. Katjitani, *J. Phys. Chem. Solids* **60**, 1431 (1999).
  - [5] P. Adelman, B. Renker, H. Schober, M. Braden, and F. Fernandez-Diaz, *J. Low Temp. Phys.* **117**, 449 (1999).
  - [6] H. Tou, Y. Maniwa, T. Koiwasaki, and S. Yamanaka, *Phys. Rev. Lett.* **86**, 5775 (2001); *Phys. Rev. B* **63**, 020508 (2000).
  - [7] T. Yokoya, Y.Ishiwata, S. Shin, S. Shamoto, K. Iizawa, T. Kajitani, I. Hase, and T. Takahashi, *Phys. Rev. B* **64**, 153107 (2001).
  - [8] R. Weht, A. Filippetti, and W.E. Pickett, *Europhys. Lett.* **48**, 320 (1999).
  - [9] I. Hase and Y. Nishihara, *Phys. Rev. B* **60**, 1573 (1999).
  - [10] P. Nozières and D. Pines, *The theory of quantum liquids* (Addison Wesley, Boston 1989).
  - [11] P.B. Visscher and L.M. Falicov, *Phys. Rev. B* **3**, 2541 (1971); A.L. Fetter, *Ann. of Phys.* **88**, 1 (1974).
  - [12] A.Abrikosov, L.Gor'kov, and I.Dzyaloshinskii, *Methods of quantum field theory in statistical physics* (Dover, New York, 1963).
  - [13] V.Z. Kresin and H. Morawitz, *Phys. Lett. A* **145**, 368 (1990).
  - [14] H. Morawitz, I. Bozovic, V.Z. Kresin, G. Rietveld, and D. van der Marel *Z. Phys. B* **90**, 277 (1993).
  - [15] A. Bill, H. Morawitz, and V.Z. Kresin, *J. Low Temp. Phys.* **117**, 283 (1999); *J. Supercond.* **13**, 907 (2000).
  - [16] W. McMillan and J. Rowell, in *Superconductivity*, edited by R. Parks (Marcel Dekker, New-York, 1969), p. 561; E. Wolf, *Principles of electron tunneling spectroscopy* (Oxford U. Press, New-York, 1985).
  - [17] G. Grimvall, *The electron-phonon interaction in metals*, *Sol. State Phys.*, vol. XVI (North-Holland, Amsterdam, 1981).